

20030109015

AD-A145 578

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER CWRU/DMS/TR-16	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (12)
Title (and Subtitle) "The Silane Interphase of Composites: Effects of Process Conditions on $\gamma$ -Aminopropyltriethoxysilane"		5. TYPE OF REPORT & PERIOD COVERED Technical Report PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) S.R. Culler, H. Ishida and J.L. Koenig		8. CONTRACT OR GRANT NUMBER(s) N00014-80C-0533
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-739
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 Quincy Street Arlington, Virginia 22217		12. REPORT DATE September 4, 1984
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 33
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; its distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC SEP 17 1984 M.A.		
18. SUPPLEMENTARY NOTES Prepared for journal publication		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) FT-IR, Silane Coupling Agent, Composite, Interphase, $\gamma$ -Aminopropyltriethoxysilane		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) SEE ABSTRACT OF PAPER		



Abstract

FT-IR spectroscopy was used to collect spectra of <sup>gamma</sup>-aminopropyltriethoxy silane (<sup>gamma</sup>-APS) coupling agent deposited on KBr plates, modelling the silane interphase of composites, to study the effects of heating the <sup>gamma</sup>-APS film under various environmental conditions. This coupling agent is used in fiber reinforced epoxy composites. An aminebicarbonate salt forms when the sample is dried in a moist carbon dioxide environment giving rise to a series of bands, from 2800 to 2000  $\text{cm}^{-1}$  and bands at 1637  $\text{cm}^{-1}$ , 1330  $\text{cm}^{-1}$ , 696  $\text{cm}^{-1}$  and 663  $\text{cm}^{-1}$ . The primary amine group is split into two bands at 1572  $\text{cm}^{-1}$  and 1486  $\text{cm}^{-1}$  in the  $\text{NH}_3^+$  form. Heating removes the aminebicarbonate salt at temperatures above 95 C and condenses the  $\gamma$ -APS polymer to a polysilsesquoxane film. The aminebicarbonate salt partially reforms if the  $\gamma$ -APS film is stored in a moist  $\text{CO}_2$  environment. At temperatures above 120 C the primary amine of  $\gamma$ -APS is oxidized in air to imine groups. In the process of evolving the  $\text{CO}_2$  the polymer is further condensed and the amine groups can be converted to imines if the temperatures exceeds 120 C, both processes reduce the reactivity of the coupling agent with the epoxy resin. The structure of the silane interphase must be controlled during the processing of the composite to yield materials with maximum properties.

### Introduction

Silane coupling agents are used to improve the hydrothermal stability of reinforced composites. Silane coupling agents also improve the adhesion of the matrix resin to the reinforcement material and aid in the transfer of stresses during the process of mechanical deformation (1). It is believed that through the control of the structure of the siloxane interphase in composites, further improvements in the mechanical and hydrothermal properties of the composite will result. Many studies have attempted to elucidate the molecular structure of the polysiloxane interphase of  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS) (2-26). The  $\gamma$ -APS coupling agent is predominately used with epoxy resins. Although  $\gamma$ -APS is one of the most studied coupling agents, it is also the one which stirs the greatest controversy over its molecular structure. Part of the problem is the variety of process conditions used in sample preparation.

In the past, many structures have been proposed for the hydrolyzed, partially-condensed form of  $\gamma$ -APS on various substrates. These previous findings have been documented in a recent review by Ishida (27). In brief, the controversy is over the structure of the amine functionality of the  $\gamma$ -APS coupling agent. Although spectra of primary amines are usually very simple (28,29), it is known that adsorbing  $\gamma$ -APS on various substrates yields very complex spectra. The controversy in the literature centered on the formation of cyclic

structures of 5 or 6 membered rings (2,10), the formation of zwitterions (10,14,15) and protonated amines (12,23-25). Little convincing evidence was presented however, until the early 1980's when Boerio et al. (17) speculated that carbon dioxide may be responsible for the complexity of the infrared spectrum of air dried  $\gamma$ -APS films. Reports appeared to support the findings that the amine group was in a protonated form (12,23-25). Naviroj et al. (18) provided evidence that  $\text{CO}_2$  was responsible for the complexities in the IR spectra by preparing films of  $\gamma$ -APS on AgBr plates under nitrogen, carbon dioxide and air environments. They reported the loss of the bands at  $1630\text{ cm}^{-1}$ ,  $1576\text{ cm}^{-1}$ ,  $1489\text{ cm}^{-1}$  and  $1330\text{ cm}^{-1}$  when the film was dried under nitrogen and an increase in these bands when the film was dried under carbon dioxide. Culler et al. (21) reported that carbon dioxide was evolved from air-dried coatings of  $\gamma$ -APS on E-glass fibers when heated above  $95^\circ\text{C}$  and that approximately half of the amine groups form an aminebicarbonate salt. The same study (21) also reported that carbon dioxide was evolved when coatings of  $\gamma$ -APS films prepared from solution pH's above 7.0 on E-glass fibers were heated. Changing the pH of the treating solution confirmed that the complexity of the NH deformation region in the infrared spectrum was due to protonated  $\text{NH}_3^+$  and the anion used. These studies support the formation of a salt with the primary amine group of  $\gamma$ -APS as the primary structure rather than the cyclic structure. Today it is believed that carbon dioxide forms with  $\gamma$ -APS at its natural pH (10.8). Although it has been suggested that an amine bicarbonate may not be formed, but instead an amine carbonate species or a carbamate is formed (26), this study

reports further evidence that an aminebicarbonate species is formed when  $\gamma$ -APS is dried in moist air or carbon dioxide environments.

Recently, it was proposed that one of the mechanisms by which these coupling agents function in composite materials is the penetration of the resin matrix into the silane interphase (1). The combination of the penetration of the resin into the physisorbed  $\gamma$ -APS forming a network and the chemical bonding theory (formation of covalent bonds to the reinforcement material and the matrix resin are needed for maximum effectiveness) are capable of explaining many of the experimental findings reported on coupling agents. If these theories are correct, then it becomes necessary to understand how the heating process necessary in curing the composite affects the structure of the silane interphase and its potential compatibility and reactivity with the resin. Typically, in the normal composite formation process the silanes are heat treated for a short period before the resin is added to condense the coupling agent to siloxane polymers. Then the resin is added and the composite is cured near 120 C. The effects of heating films of  $\gamma$ -APS with and without the epoxy resin at different temperatures are also reported.

#### Experimental

The coupling agent used in this study,  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS), was purchased from Petrarch Systems Inc. The  $\gamma$ -APS was used as received without further purification. The KBr salt plates (20 x 2.5 mm) were purchased from

Optovac and used as received. The KBr powder was purchased from Aldrich Chemical Co. with a purity of greater than 99% and was stored in a desiccator until used. The epoxy resin, Epon 828, was purchased from Miller Stevenson Co. and was stored in a refrigerator until used. The epoxy resin was used as received.

The FTS-15 Digilab FT-IR Spectrophotometer purged with dry air was employed to collect all the transmission spectra using a room temperature (TGS) detector. Between 20 and 100 scans of each sample at a resolution of 2 or 4  $\text{cm}^{-1}$  were collected. The FTS-20E Digilab FT-IR Spectrophotometer purged with nitrogen gas was employed to collect the diffuse reflectance infrared spectra using a narrow band pass mercury cadmium telluride (MCT) detector. A Digilab diffuse reflectance cell (Digilab DRA-100) with 2 hemispherical mirrors collected the diffuse reflectance spectra. KBr powder was used as the reference material so that the Kubelka-Munk reflectance plot could be produced.

For the heating studies, all samples were cast on KBr plates and heated in a Perkin-Elmer heating jacket to an accuracy of better than 0.5 C with a chromel-alumel thermal couple. Twenty scans of the sample and reference were collected for the heated samples. The powdered samples were heated in an air convection oven. The  $\gamma$ -APS films were prepared by brushing the neat liquid over a KBr plate until the coupling agent was hydrolyzed by the moisture in the atmosphere. Samples that were not air dried were prepared in a glove bag. Nitrogen gas with a purity of greater than 99.99% was used to create a

nitrogen environment. Bone dry carbon dioxide with a purity of greater than 99.99% was used to create a carbon dioxide environment.

### Results and Discussion

$\gamma$ -APS is easily hydrolyzed in water, a process that converts the three ethoxy groups to alcohols forming silanol groups on the coupling agent. The silane coupling agents are most commonly used in their hydrolyzed form and are adsorbed/deposited on the reinforcement material. The differences between the hydrolyzed and unhydrolyzed forms of  $\gamma$ -APS had previously been assigned to the formation of an amine bicarbonate salt with the primary amine group of the coupling agent. Recently, however, the correctness of this assignment has been questioned (26). It was suggested that a bicarbonate salt is not formed, but a carbonate species is instead formed when the coupling agent is condensed in air. Infrared spectroscopy can be used to address this issue as these species have distinct absorption spectra. A carbonate species always has one strong band near  $1430\text{ cm}^{-1}$  and sometimes a second band is seen in this region when the infrared spectra of carbonate salts (30,31) is obtained. If, however, a carbonyl type species was formed, then an absorbance in the 1800 to  $1650\text{ cm}^{-1}$  region of the infrared spectrum would be expected. When the infrared spectra of a bicarbonate species is obtained, there is always a band near  $1630\text{ cm}^{-1}$  and a strong band between 1300 and  $1400\text{ cm}^{-1}$ . These bands are assigned to the  $\text{OCO}_2$  symmetric stretching mode near  $1350\text{ cm}^{-1}$  and the  $\text{OCO}_2$  antisymmetric stretching mode at  $1630\text{ cm}^{-1}$  of

the bicarbonate species.

Heating experiments can also be used to test for the presence of a bicarbonate or a carbonate salt. A much higher temperature is required to decompose a carbonate species than a bicarbonate species to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (32). Culler et al. (21) previously reported that  $\text{CO}_2$  was evolved from the air dried samples of  $\gamma$ -APS at temperature above 95 C, a temperature at which the carbonate species would be stable. Figure 1 shows the effect of heating  $\gamma$ -APS on a KBr plate at 120 C as a function of time. The film of  $\gamma$ -APS was air hydrolyzed on the KBr plate and is approximately 0.4 microns thick. Spectrum A of Figure 1 is the coupling agent condensed in air overnight. Spectra B through E are the same sample of  $\gamma$ -APS on the KBr plate heated at 120 C for different lengths of time in a heating cell. After 30 minutes at 120 C the IR spectrum of the  $\gamma$ -APS film has dramatically changed from the complicated Spectrum A of the air hydrolyzed, nonheated sample. The bands at 1330, 1567, 1488 and 1631  $\text{cm}^{-1}$  have disappeared, along with the background in Spectra A from 3600 to 2700  $\text{cm}^{-1}$  which is characteristic of a salt and hydrogen bonded Si-OH groups of the coupling agent. Spectrum E of the heated sample shows an equal intensity of the Si-O-Si bands near 1100  $\text{cm}^{-1}$  and no evidence of any Si-OH is seen between 3450  $\text{cm}^{-1}$  and 3025  $\text{cm}^{-1}$  as in the partially condensed polymer film or near 960  $\text{cm}^{-1}$ . This indicates that the siloxane polymer film is now highly condensed under these heating conditions. The tentative band assignments for the hydrolyzed/partially condensed silane coupling agent and same sample

heated for 30 mins at 120 C are shown in Table 1. When the salt has been removed, there is one band in the NH deformation region near 1500  $\text{cm}^{-1}$  which is attributed to the free  $\text{NH}_2$  band of a primary amine. These results can be interpreted as the loss of carbon dioxide from the amine group of  $\gamma$ -APS and condensation of silanol groups to siloxanes. From the changes in the spectra of Figure 1, the time for the carbon dioxide to be evolved is between 15 and 30 minutes for this sample. The precise time depends upon the thickness of the  $\gamma$ -APS film. In general, when  $\gamma$ -APS from a typical treating solution of 1% or less by weight is used to treat E-glass fibers it will require less than 5 minutes at 100 C to remove the salt (21).

The changes occurring upon heating the partially cured film of  $\gamma$ -APS for 30 mins. at 120 C are more clearly shown in the difference spectrum in Figure 2. The spectrum of the heated film of  $\gamma$ -APS on a KBr plate was subtracted from the spectrum of the air hydrolyzed sample revealing a spectrum characteristic of a bicarbonate species which forms with the  $\gamma$ -APS coupling agent. This bicarbonate is shown by the presence of the bands at 1637  $\text{cm}^{-1}$ , 1565  $\text{cm}^{-1}$ , 1486  $\text{cm}^{-1}$ , 1329  $\text{cm}^{-1}$ , the weak series of bands from 2350  $\text{cm}^{-1}$  to 2100  $\text{cm}^{-1}$  and the appearance of new bands at 697  $\text{cm}^{-1}$ , 668  $\text{cm}^{-1}$  and 495  $\text{cm}^{-1}$ . These bands are all consistent with the formation of an aminebicarbonate salt species. The two new bands at 697  $\text{cm}^{-1}$  and 668  $\text{cm}^{-1}$  are assigned to the bicarbonate salt and the 495  $\text{cm}^{-1}$  is the combination of  $\text{NH}_3^+$  torsional oscillation and asymmetric  $\text{NH}_3^+$  deformation. The two bands at 697  $\text{cm}^{-1}$  and 668  $\text{cm}^{-1}$  are the most characteristic of a bicarbonate

species (28). Also the difference spectrum clearly shows the broad hydrogen bonded Si-OH bands from  $3621\text{ cm}^{-1}$  to  $3250\text{ cm}^{-1}$  have disappeared from the heated sample. Heating is known to reduce hydrogen bonding (28,29).

The stability of  $\gamma$ -APS to heating was studied and is discussed in the following section. The  $\gamma$ -APS was hydrolyzed in distilled water and allowed to air dry, modelling the physisorbed layers of silane coupling agent on a surface (18). Transparent KBr pellets of these samples were made. The results of performing this experiment as a function of the heating temperature are shown in Figure 3. The bicarbonate salt bands are present in all the samples except when the sample was heated for 3 hours at 160 C. These findings are in conflict with the previous results for  $\gamma$ -APS on a substrate (21). Even after heating at 120 C for 3 hours all of the bicarbonate salt was still present a result not seen in Figure 1 when the  $\gamma$ -APS was cast on a KBr plate.

Diffuse reflectance, (DRIFT), a technique that is ideal to study powders, was used to further study the effects of heating  $\gamma$ -APS. The same sample preparation procedure was repeated. The results using the DRIFT technique are shown in Figure 4. None of the bicarbonate salt is removed at 80 C. When a temperature of 120 C was reached all of the bicarbonate salt is removed, however at the highest temperature (160 C) the formation of a new band is seen at  $1661\text{ cm}^{-1}$ . These results are in agreement with the results obtained in Figure 1. The results shown in Figures 4 and 5 are clearly contradictory for the

same compound. This is a clear example of how the process of preparing the sample for infrared analysis can mask the actual results (33). In the process of grinding the sample with KBr to make pellets the carbon dioxide and moisture from the atmosphere reforms the bicarbonate salt. This grinding process increases the surface area of the coupling agent exposed to air. The extra moisture explains why the spectra show that the bicarbonate salt is still present even though they have been heated for 3 hours up to 120 C, conditions which clearly removed the salt in the other experiments. It is also of interest to note that transparent KBr pellets greatly diminish the salt bands between 2800 to 2000  $\text{cm}^{-1}$  adding to the confusion over the detection of the bicarbonate species. The results of the heating experiments support the claim that an amine bicarbonate salt is indeed formed when  $\gamma$ -APS is hydrolyzed and condensed in a humid air environment.

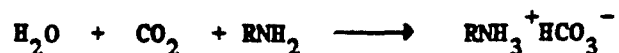
In the spectrum of the samples heated at 160 C very little bicarbonate salt is present, but a new band is seen at 1661  $\text{cm}^{-1}$ . This band is in the proper location to be an imine (C=N) (28,29). If this interpretation is correct, then the primary amine is oxidized to an imine group during the heating process.

Silane coupling agents not only improve the hydrothermal stability of reinforced composites, they also aid in the interaction with the resin matrix through chemical reaction or mechanical interlocking. Therefore, it is necessary to understand how heating affects the molecular structure of the  $\gamma$ -APS interphase in order to

predict which conditions will result in the most favorable interaction between the resin matrix (epoxy) and the amine coupling agent. The evolution of the bicarbonate salt is thought to be desirable, as more of the amine groups are available to react with the epoxide groups of the epoxy resin. According to the chemical bonding theory, a chemical reaction between the matrix resin and the coupling agent is needed for the hydrothermal stability and mechanical properties of composites. However, the evolution of the bicarbonate salt does not ensure that the primary amine groups will be free as seen by the results of preparing KBr pellets with heated powders of  $\gamma$ -APS. When the heat treated samples are exposed to atmospheric conditions, some of the bicarbonate salts reform with the coupling agent. This is shown in Figure 5 where the reformation of the bicarbonate bands are viewed over the time that a  $\gamma$ -APS film on a KBr salt plate was exposed to air. One can see that not all of the amine groups that originally had a bicarbonate salt, reformed the salt. The intensity of the  $1330\text{ cm}^{-1}$  band can be used to monitor this reaction. In general, not more than 25 percent of the salt is reformed. Also the intensity of the Si-O-Si bands near  $1100\text{ cm}^{-1}$  are different. In the CH stretching region only the low frequency side ( $3100$  to  $2300\text{ cm}^{-1}$ ) shows the distortion of the reformed salt. This indicates that there are very few Si-OH groups left (seen near  $3450\text{ cm}^{-1}$ ) after heating.

Since the bicarbonate salt can reform with the primary amines of the  $\gamma$ -APS film, it is of interest to know the conditions necessary for this process to occur. Two experiments were performed to address this

issue. In both experiments the bicarbonate salt was evolved by heating the  $\gamma$ -APS film at 110 C for 30 minutes. One sample was placed in a glove bag with a  $\text{CO}_2$  and moist  $\text{N}_2$  purge. The other sample was placed in a glove bag with only a dry  $\text{CO}_2$  gas purge. The results of these two experiments are shown in Figures 6 and 7. The bicarbonate salt reforms within 2.5 hours in the moist carbon dioxide atmosphere but does not reform within 2 hours in the dry  $\text{CO}_2$  atmosphere. These results indicate that moisture must be present for the salt to reform. The necessity of water or moisture to reform the salt bands with the amines of the  $\gamma$ -APS film.



This is consistent with the interpretation of bicarbonates and not just carbonates being responsible for the complexity of the infrared spectra of air dried films of  $\gamma$ -APS.

During the course of this study, the reformation of the bicarbonate salt with the primary amine group was observed to be a function of the film thickness. The thinner the film of  $\gamma$ -APS, the faster the bicarbonates salt reformed. It was also interesting to note that under normal atmospheric conditions, not more than 35% of the original salt ever reformed. This difference must be due to the total condensation of the polymer film in which fewer of the primary amine groups are available to react with moisture and carbon dioxide. The corollary of this process was also observed. The process of

removing the bicarbonate salt is a function of the film thickness at a given temperature between 90 C and 120 C. We want to document the fact that temperatures above 90 C are needed to evolve the bicarbonate salt, but heating does not ensure that the salt will not reform. The reformation of the salt after heating depends on the environment of the sample before it is used in the composite.

The hypothesis that the primary amine of  $\gamma$ -APS is oxidized to an imine can be easily tested by performing the heating experiment in a nitrogen atmosphere. The results of heating the coupling agent on a KBr plate under a nitrogen atmosphere are shown in Figure 8. A very weak band at  $1661\text{ cm}^{-1}$  is present, but does not increase in intensity as a function of time heated. It can be inferred from the results shown in Figures 6 - 8 that the following reaction has occurred to degrade the primary amine of the coupling agent to an imine (34):



The oxidation of the amine groups is undesirable because it will reduce the reactivity of the coupling agent with the epoxy resin because one of the active hydrogens of the amine is used up in the process of forming the imine group.

Second derivative spectroscopy (35,36) was used to locate the presence of bands in the  $1700$  to  $1365\text{ cm}^{-1}$  region of overlapping bands. Any imine present in the air dried samples before heating would be observable. The results are shown in Figure 9. The band at

1661  $\text{cm}^{-1}$  is overlapped with the bicarbonate band near 1637  $\text{cm}^{-1}$ . When the second derivative is taken and smoothed to reduce the noise as shown in Spectrum B of Figure 9, a minimum appears in the curve at 1661  $\text{cm}^{-1}$ . This indicates that a small amount of the imine is present even when the sample has not been heated. It is this amount of imine which gives rise to the weak band at 1661  $\text{cm}^{-1}$  in the spectrum in Figure 6 prepared under a nitrogen atmosphere. The other minima in spectrum B occur at 1642  $\text{cm}^{-1}$ , 1627  $\text{cm}^{-1}$ , 1572  $\text{cm}^{-1}$ , 1547  $\text{cm}^{-1}$ , 1520  $\text{cm}^{-1}$ , 1490  $\text{cm}^{-1}$ , 1433  $\text{cm}^{-1}$ , and 1384  $\text{cm}^{-1}$ . The minimum at 1642  $\text{cm}^{-1}$  corresponds to the  $\text{OCO}_2$  asymmetric stretching mode. The minima at 1572 and 1490  $\text{cm}^{-1}$  correspond to the  $\text{NH}_3^+$  modes of the aminebicarbonate salt. Three new bands appear from this analysis at 1627  $\text{cm}^{-1}$ , 1547  $\text{cm}^{-1}$  and 1520  $\text{cm}^{-1}$ . The band at 1627  $\text{cm}^{-1}$  can be attributed to the hydrogen bonded  $\text{NH}_2$  groups of  $\gamma$ -APS, because hydrogen bonding will shift the NH deformation band to higher wavenumbers (28). The appearance of the hydrogen bonded  $\text{NH}_2$  groups is consistent with the fact that no band is seen at 1600 in the partially condensed film of  $\gamma$ -APS. Culler et al. (21) previously reported that only half of the primary amine groups form the bicarbonate structure. The two minima at 1547 and 1520  $\text{cm}^{-1}$  are likely due to another form of  $\text{NH}_3^+$  with the anion being weaker than the bicarbonate salt explaining the smaller splitting of these two bands.

The time required to convert the primary amines to imines was studied. This is shown in Figure 10 when a film of  $\gamma$ -APS is heated at 150 C for 15 mins. The  $\gamma$ -APS film turned yellow. It is evident that

nearly all of the primary amines (band at  $1602\text{ cm}^{-1}$ ) have been converted to imines (band at  $1661\text{ cm}^{-1}$ ). Therefore, when  $\gamma$ -APS is used as the coupling agent, it is important to keep the cure temperature below  $120\text{ C}$  in air, otherwise the probability of having a chemical reaction with the resin matrix will be drastically reduced. A secondary effect of heat treatments is to condense the silanols in both the chemisorbed and physisorbed layers to the polysiloxane structure. This is also an undesirable because it inhibits the interpenetration of the siloxane interface by the resin which the interpenetration theory states is vital. Interpenetration would be decreased if the coupling agent structure was highly crosslinked as it is when cured (no Si-OH seen).

Therefore, several competing processes are occurring in the  $\gamma$ -APS system: a) the bicarbonate salt reacts with approximately 50% of the primary amines; b) in the process of removing the bicarbonate salt the silane interphase is further condensed; c) when the temperature is too high ( $120\text{ C}$  and above) the primary amine is readily oxidized to an imine; d) the ability of the resin matrix to interact (chemically or by mechanical penetration) with the silane coupling agent is reduced. These factors must be carefully controlled to optimize the interphase region of reinforced composites when the coupling agent used is  $\gamma$ -APS.

The reaction between the  $\gamma$ -APS coupling agent and an epoxy resin was studied at 120 C between KBr plates. The coupling agent was preheated to 120 C for several minutes to condense the Si-OH groups to siloxanes. Then the epoxy resin was added. This procedure was chosen because it models the actual processes used in the industrial manufacturing of the reinforced composites. The reaction with the epoxy resin was studied at 120 C by FT-IR for two hours. A spectrum was collected every 5 minutes for the first 50 minutes, and then every 10 minutes thereafter. From the series of spectra shown in Figure 11 it is seen that the major change occurring is the formation of a band at  $1661\text{ cm}^{-1}$ . A band in this region of the spectrum has often been assigned to the formation of an amide band when the system has been cured in the presence of accelerators and curing agents (37). However, these chemicals are not present in this study. The area of the  $1661\text{ cm}^{-1}$  band is plotted versus the time of the reaction at 120 C in Figure 12. From this plot it is apparent that the formation of the  $1661\text{ cm}^{-1}$  band is a first order reaction process. These spectra also indicate that very little epoxy was converted to a secondary amine group and an alcohol (area of the  $915\text{ cm}^{-1}$  epoxy ring band changed only (34%). Instead the primary amine groups of the coupling agent were converted to imine groups in the process of the heating experiment. Under these reaction conditions the conversion of the amine to imines is faster than the reaction of the amines with the epoxides of the epoxy resin. After 2 hours at 120 C nearly all of the amines are converted to imines. One possible process to prevent this reaction from occurring in a n industrial setting would be to prepare

the composites under vacuum conditions so that oxygen is not present in the system.

### Conclusions

$\gamma$ -APS coupling agent forms a bicarbonate salt with approximately half of the amine groups. The use of KBr pellets to study the infrared spectra of the  $\gamma$ -APS coupling agent is inappropriate because the moisture in the KBr salt and carbon dioxide in the air combine to mask the "real" structure of the coupling agent. The bicarbonate salt is easily removed from the amine groups by heating the  $\gamma$ -APS film at temperatures above 95 C. The time required to remove the bicarbonate salt from a  $\gamma$ -APS sample depends on the thickness of the sample and the heating temperature. In the process of removing the salt, the silanols become highly condensed to polysiloxanes. The bicarbonate salt, once removed by heating, will partially reform if the samples are stored in the presence of moisture and carbon dioxide. The extent of the reformation of the bicarbonate salt depends on the thickness of the  $\gamma$ -APS film and the length of time the film is exposed to atmospheric conditions. The temperature used to cure the composite (after resin is added) is critical when the coupling agent is  $\gamma$ -APS and the composite is cured under atmospheric conditions. At temperatures above 120 C, the primary amine of  $\gamma$ -APS is readily oxidized to an imine group which does not react with the epoxy groups. If the reaction with the epoxy resin is to be maximized it is necessary to control these variables which greatly affect the

structure of the silane interphase and its ability to bond to the resin. Such control should lead to improved composites with better hydrothermal stability.

Acknowledgements

The authors greatly acknowledge that this study was supported in part by a grant from the Office of Naval Research.

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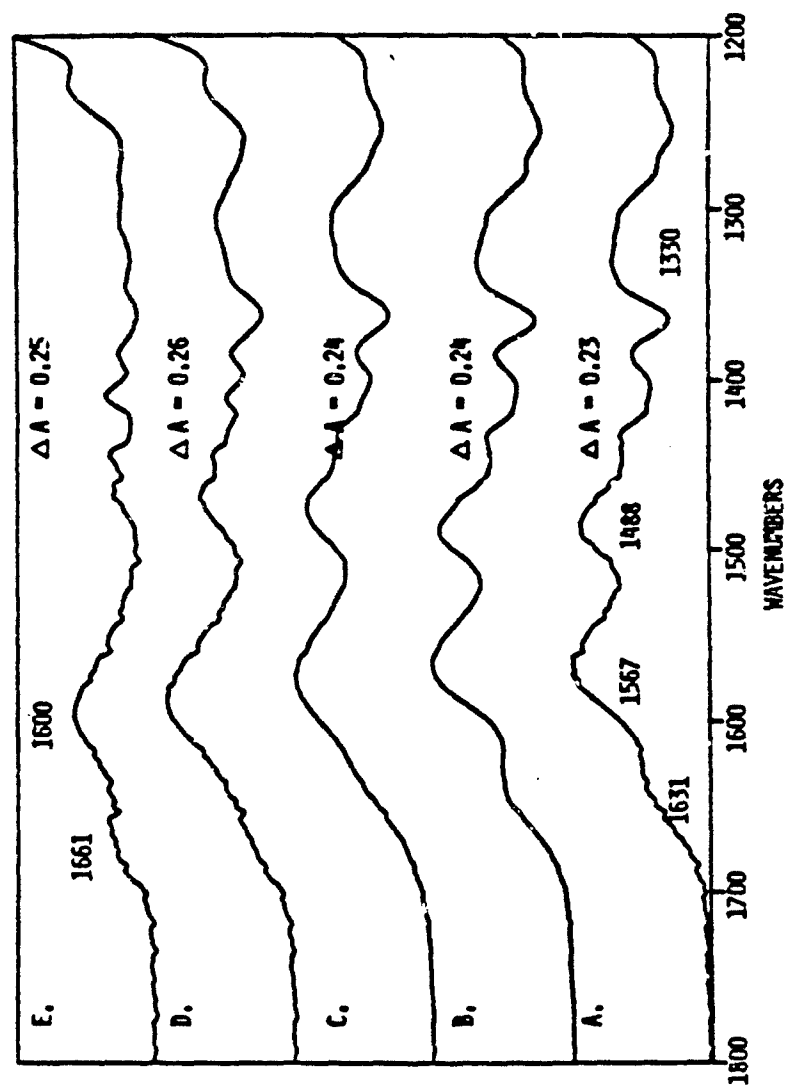


Figure 1. FT-IR spectra of a thin film of  $\gamma$ -APS (0.4 $\mu$ ) on a KBr plate; A) air dried film; B) heated no time at 120 C; C) heated 5 mins. at 120 C; D) heated 15 mins. at 120 C; E) heated 30 mins. at 120 C.

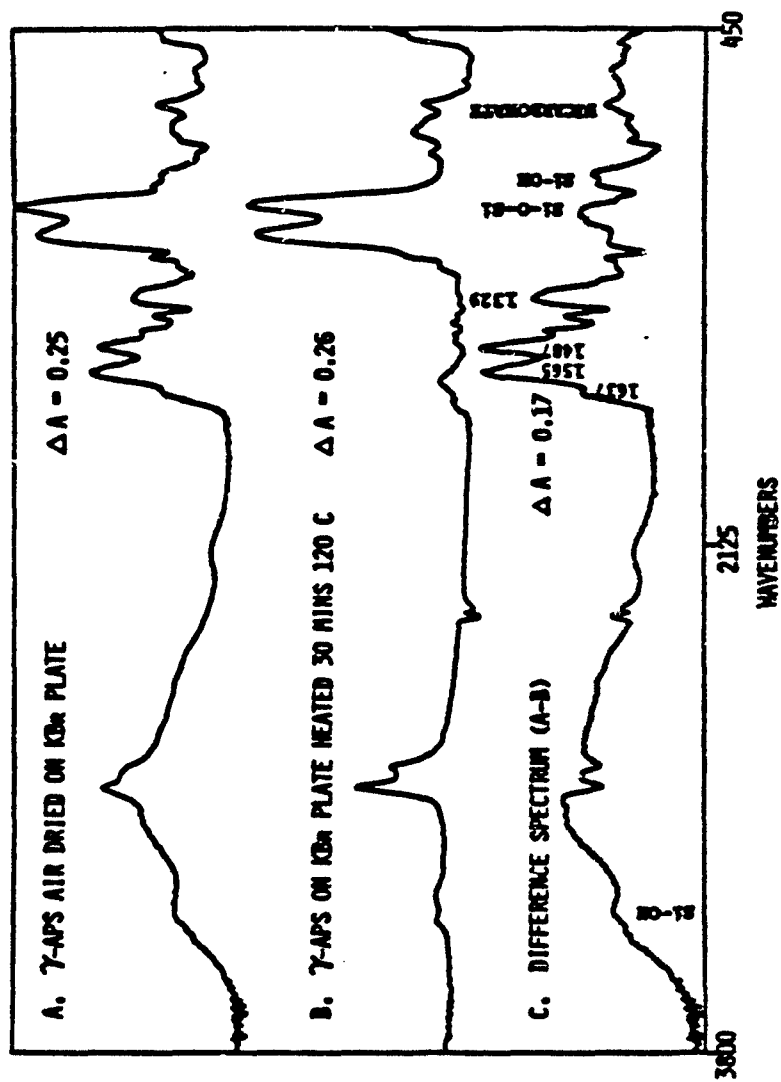


Figure 2. FT-IR transmission spectra A) air dried sample on KBr plate, B) sample heated 110 C for 30 mins. C) difference spectrum of (A - B) highlighting the changes upon heating the coupling agent.

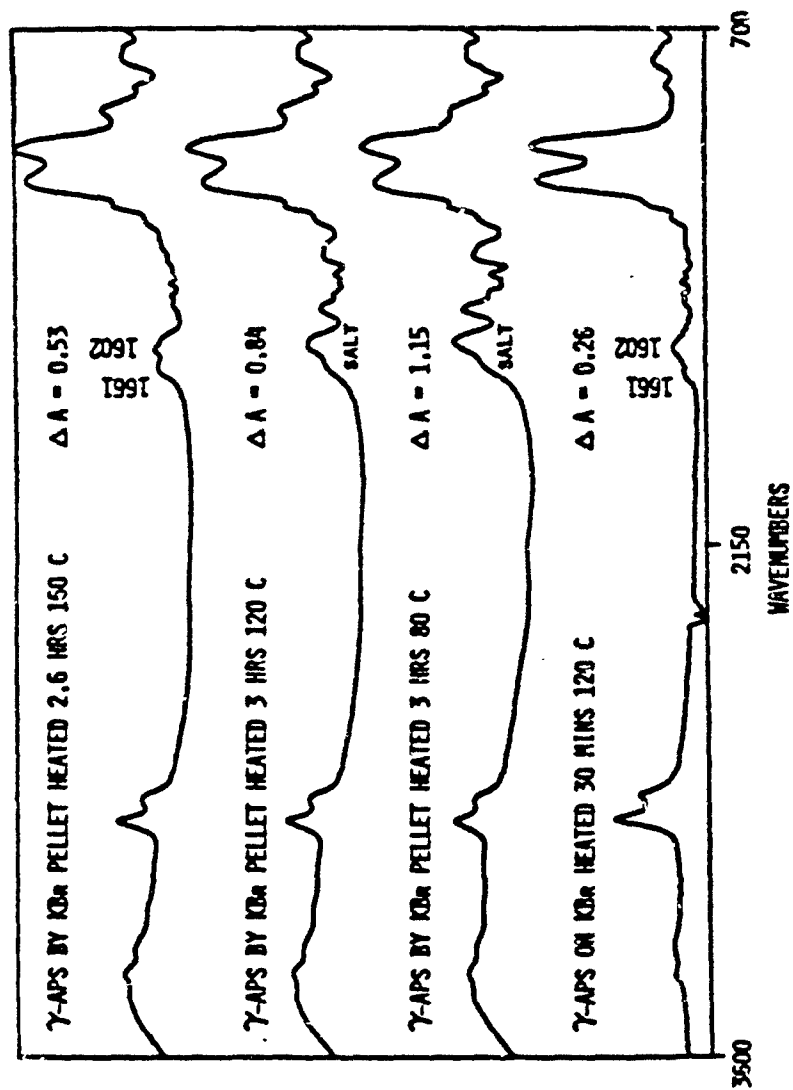


Figure 3. FT-IR transmission spectra of air hydrolyzed  $\gamma$ -APS powder prepared as KBr pellets. A) air dried, B) heated 80 C for 3 hrs, C) heated 120 C for 3 hrs. and D) heated 160 C for 2.6 hrs.

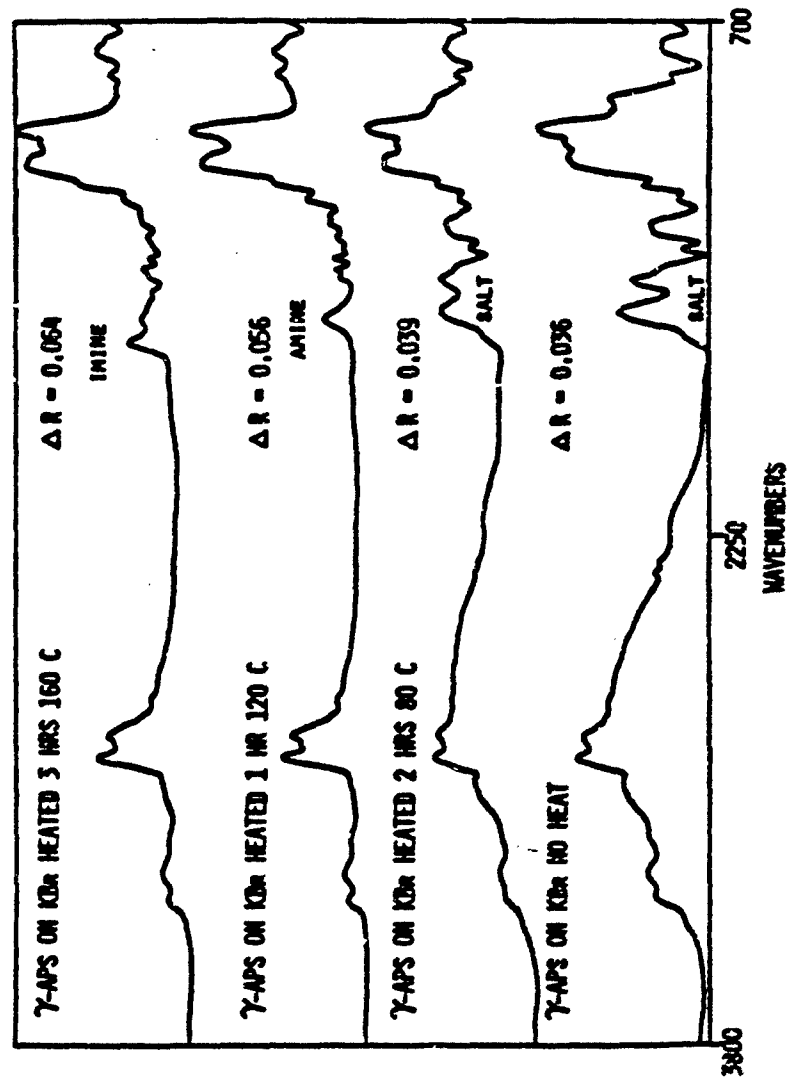


Figure 4. DRIFT spectra of  $\gamma$ -APS powders air hydrolyzed mixed with KBr powder. A) air dried, B) heated 50 C for 2 hrs., C) heated 120 C for 1 hr. and D) heated 160 C for 3 hrs.

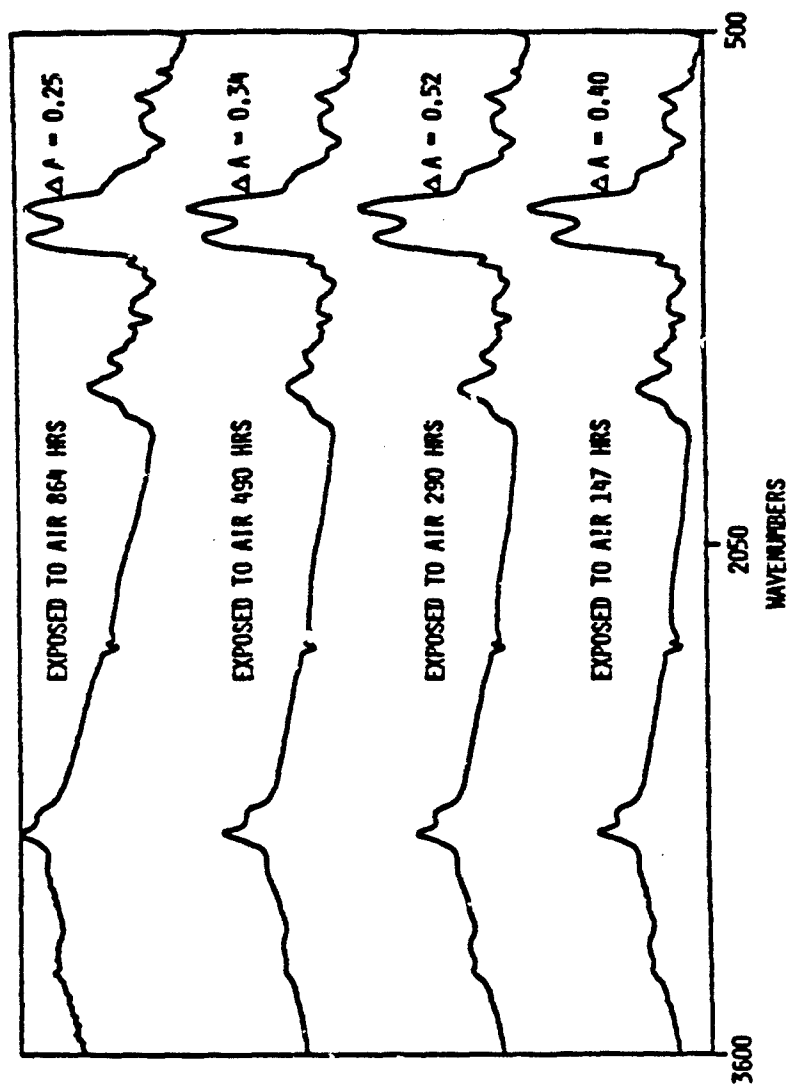


Figure 5. FT-IR transmission spectra of  $\gamma$ -APS films heated at 120 C exposed to atmospheric conditions for: A) 147 hrs., B) 290 hrs., C) 490 hrs. and D) 864 hrs.

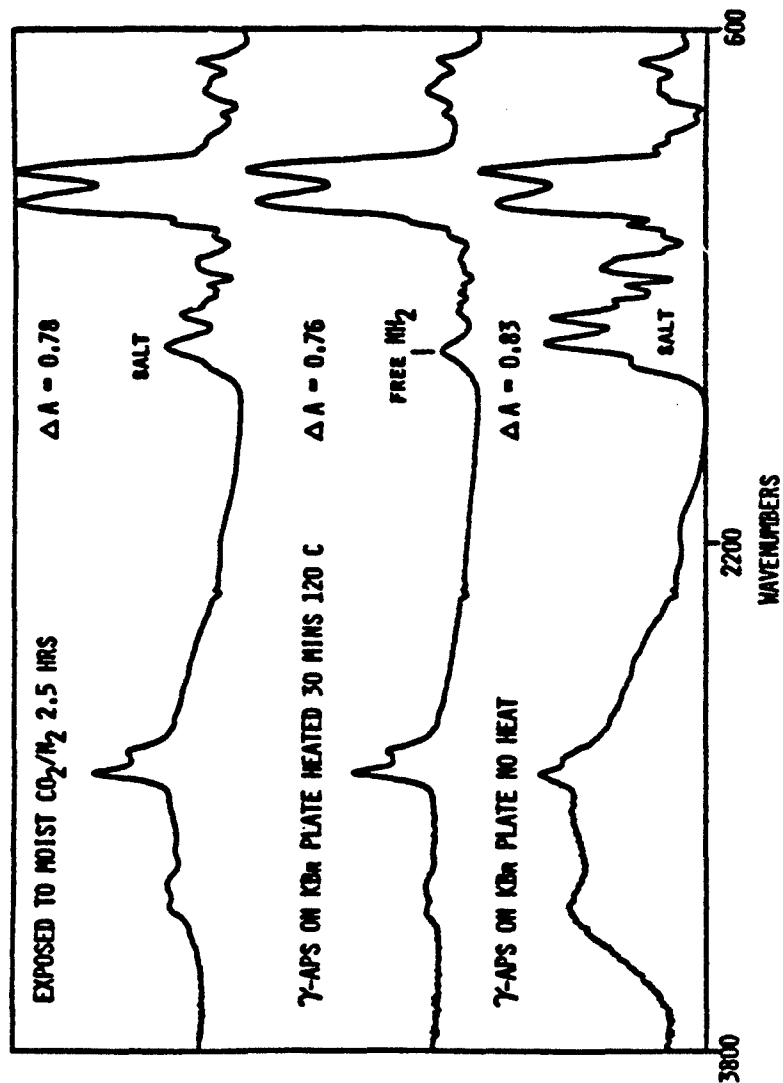


Figure 6. FT-IR transmission spectra of A) heated  $\gamma$ -APS film on a KBr plate at 110 C for 30 mins. exposed to moist nitrogen/carbon dioxide environment for B) 30 mins. and C) 2.5 hrs.

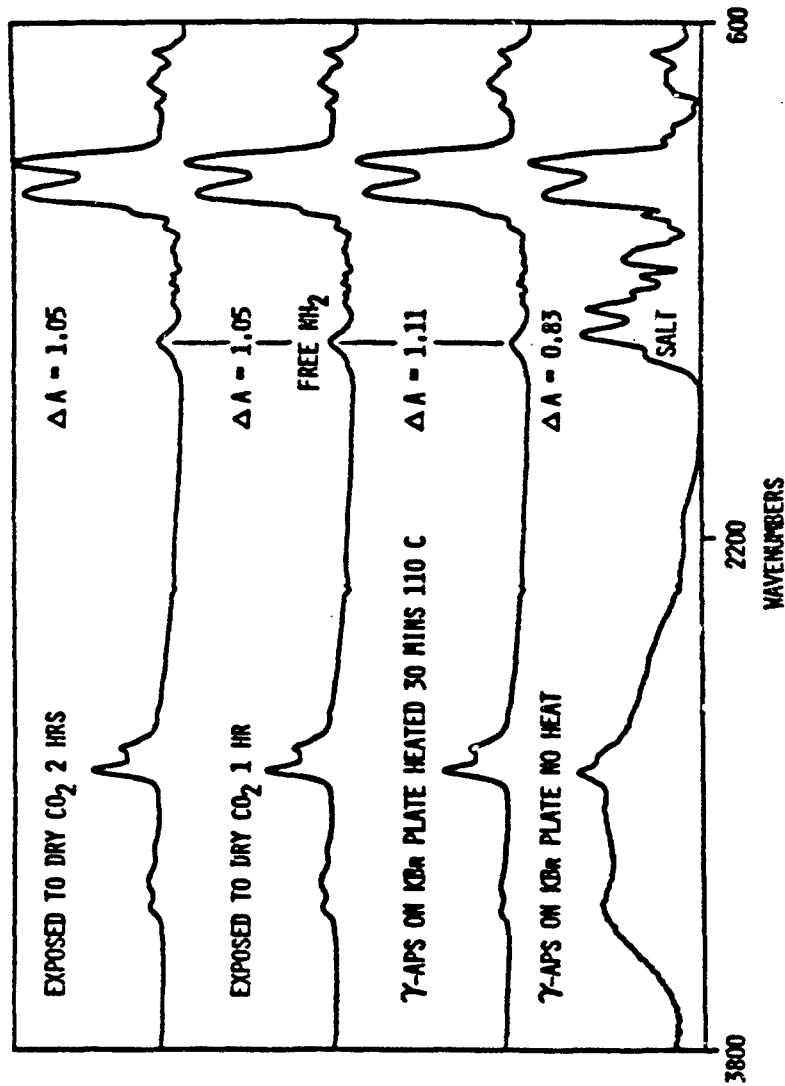


Figure 7. FT-IR transmission spectra of A) heated  $\gamma$ -APS film on KBr plate at 110 C for 30 mins. and exposed to bone dry carbon dioxide environment for B) 1 hr. and C) 2 hrs.

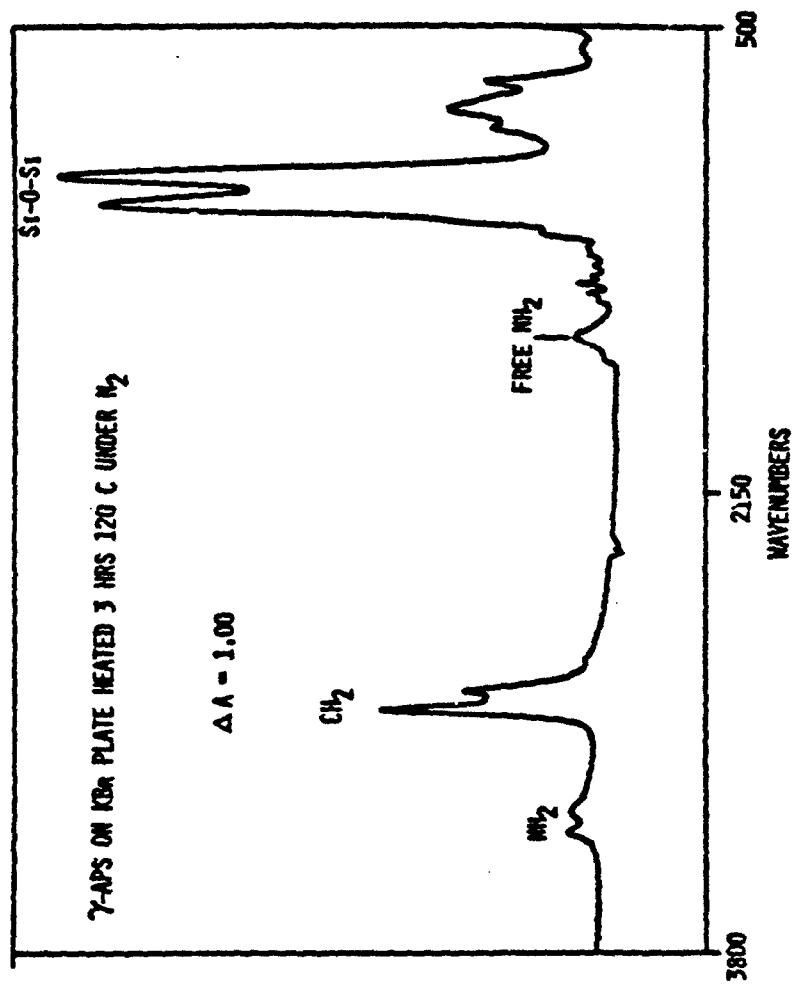


Figure 8. FT-IR transmission spectrum of a film of  $\gamma$ -APS on a KBr plate heated under a nitrogen environment for 2 hours at 120 C.

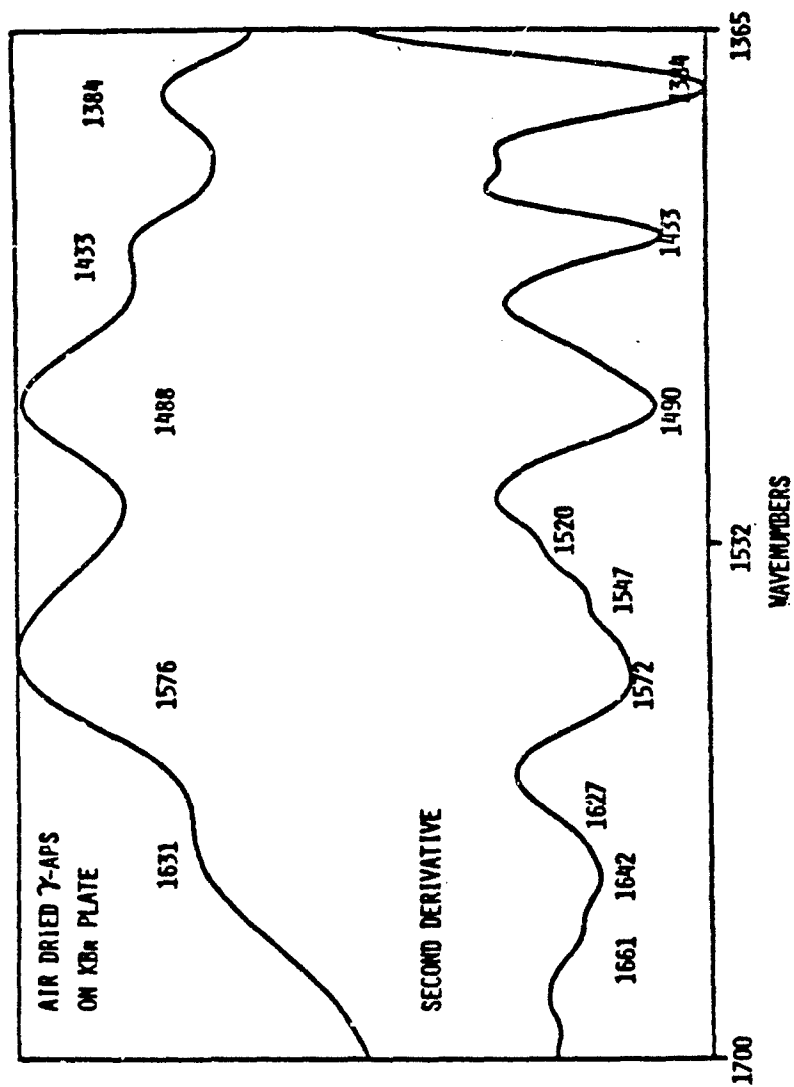


Figure 9. A) FT-IR transmission spectrum of a film of  $\gamma$ -APS on a KBr plate air hydrolyzed and dried and B) the second derivative spectrum of A smoothed by a factor of twenty to reduce the noise.

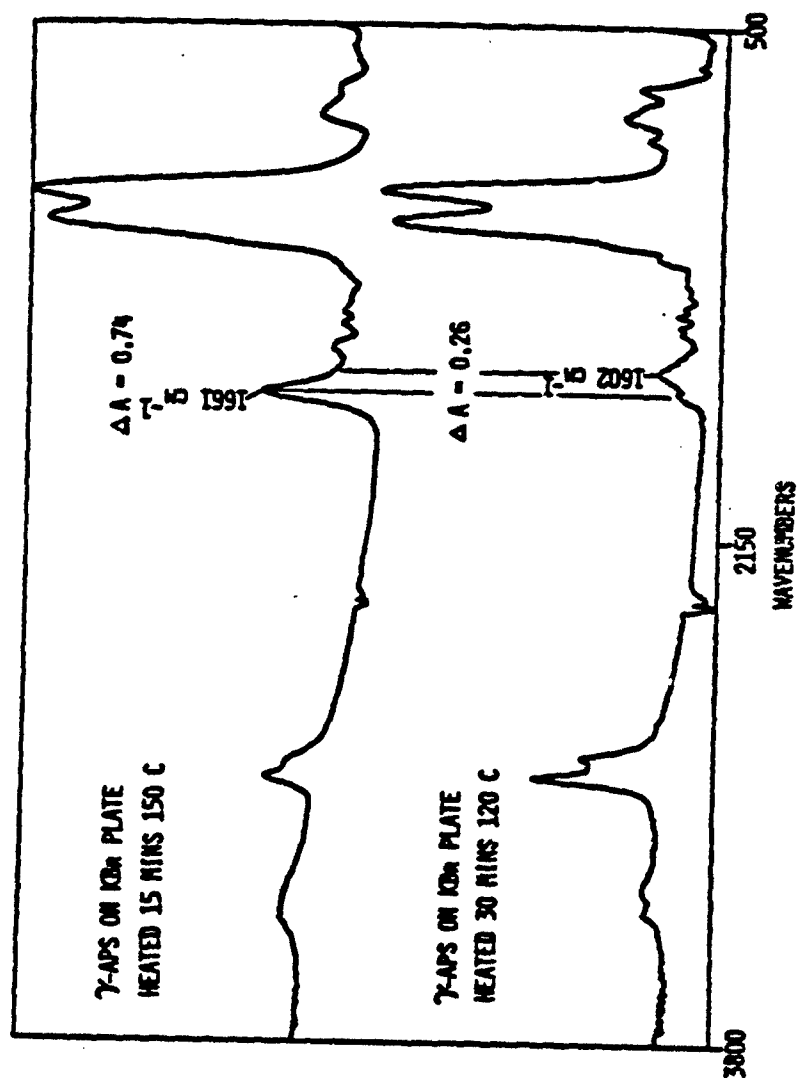


Figure 10. FT-IR transmission spectra of  $\gamma$ -APS on KBr plates heated at A) 110 C for 30 mins. and B) 150 C for 15 mins.

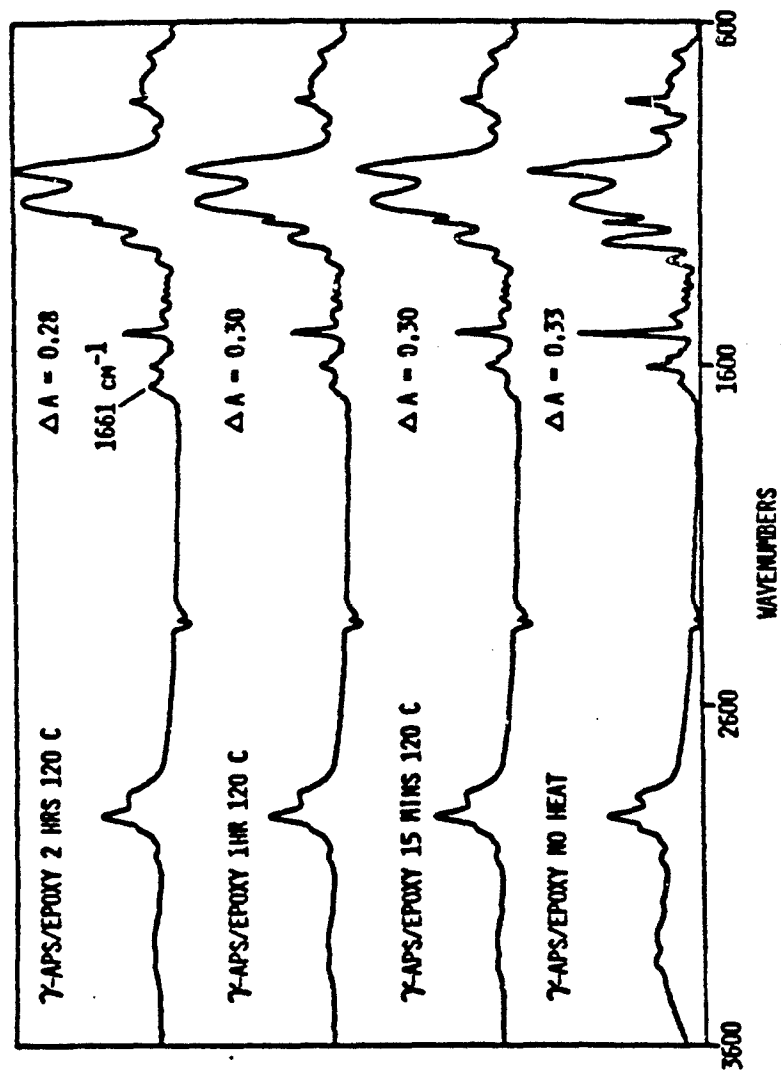


Figure 11. FT-IR transmission spectra of  $\gamma$ -APS/epoxy on a KBr plate heated at 120 C for A) initially B) 15 mins., C) 1 hr. and D) 2 hrs.

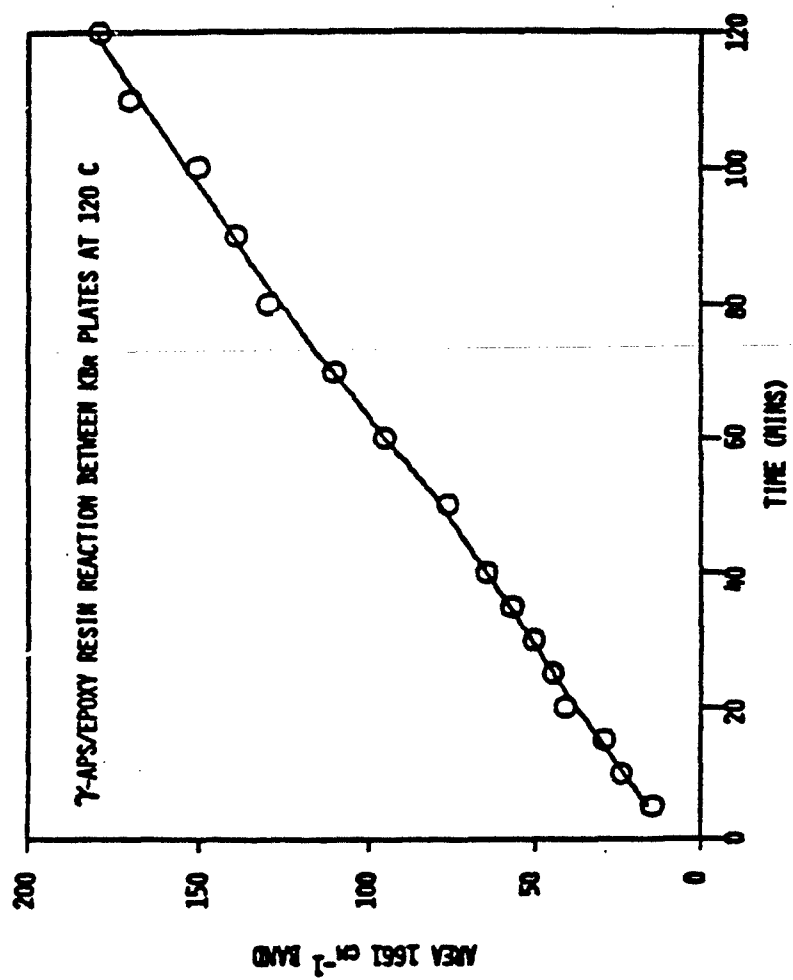


Figure 12. Plot of the integrated area of the 1661  $\text{cm}^{-1}$  band formed from the reaction of 7-APS with epoxy at 120 C versus time.

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